



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 899 297 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

03.03.1999 Bulletin 1999/09

(51) Int. Cl.⁶: **C08L 21/00**

(21) Application number: **98115684.7**

(22) Date of filing: **20.08.1998**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **26.08.1997 US 920109**

(71) Applicant:

**THE GOODYEAR TIRE & RUBBER COMPANY
Akron, Ohio 44316-0001 (US)**

(72) Inventors:

- **Sandstrom, Paul Harry
Tallmadge, Ohio 44278 (US)**
- **Blok, Edward John
Wadsworth, Ohio 44281 (US)**
- **Verthe, John Joseph
Kent, Ohio 44240 (US)**

(74) Representative: **Leltz, Paul**

**Goodyear Technical Center-Luxembourg
Patent-Department
L-7750 Colmar-Berg (LU)**

(54) **Pneumatic tire having a tread compound containing high levels of low TG polymer and resin**

(57) The present application relates to a pneumatic tire having a tread containing (a) from 50 to 90 phr (parts by weight of rubber per 100 total parts of rubber) of a rubber which, in its uncured state, has a glass transition temperature in the range of from -80°C to -110°C and (b) from 15 to 50 phr of a resin.

EP 0 899 297 A2

DescriptionBackground of the Invention

- 5 [0001] The present invention relates to a pneumatic tire having a tread which is composed of high levels of a low Tg polymer and resin. The tread composition exhibits improved lab properties which correlate to improved treadwear with concomitant improvements in traction and handling.

Summary of the Invention

- 10 [0002] The present invention relates to a pneumatic tire having a tread containing (a) from 50 to 90 phr (parts by weight of rubber per 100 total parts of rubber) of a rubber which, in its uncured state, has a glass transition temperature in the range of from -80°C to -110°C and (b) from 15 to 50 phr of a resin.

15 Detailed Description of the Invention

[0003] There is disclosed a pneumatic tire having an outer circumferential tread where said tread is a sulfur-cured composition comprising

- 20 (a) 50 to 90 phr of a rubber which, in its uncured state, is characterized by having a glass transition temperature (Tg) in the range of from -80°C to -110°C;
 (b) 10 to 50 phr of at least one rubber, each one of which, in its uncured state, is characterized by having a glass transition temperature in the range of from -79°C to +20°C and which is selected from the group consisting of natural rubber, synthetic cis 1,4-polyisoprene, 3,4-polyisoprene, styrene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubber, solution-polymerized polybutadiene rubber, emulsion-polymerized polybutadiene,
 25 isoprene/butadiene rubber and mixtures thereof; and
 (c) 15 to 50 phr of a resin selected from the group consisting of hydrocarbon resins, phenol/acetylene resins, rosin-derived resins and mixtures thereof.

- 30 [0004] The term "Tg" refers to the glass transition temperature of the identified rubber and is suitably determined by a differential scanning calorimeter at a rate of 10°C per minute.

- [0005] The tread is comprised of 50 to 90 parts by weight per 100 total parts by weight of rubber in the tread of a rubber which, in its uncured state, has a Tg in the range of from -80°C to -110°C. Preferably, the Tg of this rubber ranges from about -90 to -105°C. As used herein, this rubber is known as a low Tg rubber. Preferably, the low Tg rubber is
 35 present in an amount ranging from 50 to 70 phr. This rubber may also be characterized by a butadiene content of at least 70 weight percent or greater. Should the butadiene content be substantially less than 70 weight percent, the Tg of the rubber will not be within the desired -80 to -110°C. Preferably, the butadiene content ranges from about 75 to 100 weight percent. A representative rubber is a polybutadiene rubber having 95 weight percent or more cis 1,4-structure, a Tg of from -95 to -105°C and a Mooney viscosity (ML 1+4) at 100°C of from 30 to 100. Another example of a suitable
 40 rubber is an isoprene/butadiene copolymer rubber prepared by neodymium catalysis and characterized by having an isoprene content of about 20 weight percent, a Tg of about -90°C and a Mooney viscosity (ML1+4) at 100°C of 82. Yet another example is an isoprene/butadiene copolymer rubber prepared by neodymium catalysis and characterized by having an isoprene content of about 10 weight percent, a Tg of about -98°C and a Mooney viscosity (ML1+4) at 100°C of 82. Other examples of suitable rubbers are solution-polymerized styrene/butadiene copolymer rubbers containing up
 45 to 10 weight percent of styrene. Such styrene/butadiene copolymers exhibit a Tg of from -93°C to -80°C and Mooney viscosities (ML 1+4) at 100°C from 30 to 100. The preferred rubber is the above-described cis-1,4-polybutadiene.

- [0006] In addition to the low Tg rubber, the tread also contains from 10 to 50 phr of at least one rubber which, in its uncured state, has a Tg of from -79°C to +20°C. Preferably, from 30 to 50 phr of the total rubber in the tread is a rubber having a Tg of from -79°C to +20°C. The preferred Tg range for this rubber ranges from -50 to +10°C. The rubbers in
 50 this broad range of Tgs can be further classified as "medium Tg" rubber and "high Tg" rubber. Medium Tg rubbers are those rubbers, in their uncured state, which have a Tg ranging from -79°C to -50°C. High Tg rubbers are those rubbers having a Tg ranging from -49°C to +20°C.

- [0007] Representative examples of medium Tg rubbers include cis 1,4-polyisoprene. The cis 1,4-polyisoprene rubber includes both natural and synthetic rubbers. The cis 1,4-polyisoprene rubber, natural or synthetic, typically has a cis
 55 1,4-content of about 96 to about 99 weight percent. Synthetic cis 1,4-polyisoprene generally has a Tg of about -65°C. Natural rubber typically has a Tg of about -65°C. Typical Mooney viscosities (ML 1+4) at 100°C for synthetic cis 1,4-polyisoprene and natural rubber range from 30 to 100. Another medium Tg rubber is an isoprene/butadiene copolymer rubber prepared by neodymium catalysis characterized by an isoprene content of about 70 weight percent, a Tg of

about -79°C and a Mooney viscosity (ML1+4) at 100°C of 76. Another medium Tg rubber is solution-polymerized styrene/butadiene copolymer rubber having a styrene content of about 18 weight percent, a vinyl content of about 10 weight percent, a Tg of about -78°C and a Mooney viscosity (ML1+4) at 100°C of 85. Another example of a medium Tg rubber is a solution-polymerized polybutadiene having a vinyl content of about 45 weight percent, a Tg of about -55°C and a Mooney viscosity (ML 1+4) at 100°C of 60. Yet another example of a medium Tg rubber is a solution-polymerized trans 1,4-polybutadiene having a weight percent content of 1,4-bonds ranging from about 60 to 80 weight percent, a Tg of about -70°C and a Mooney viscosity (ML 1+4) at 100°C of 60.

[0008] Representative examples of high Tg rubbers include 3,4 polyisoprene which typically contains about 65 weight percent 3,4-isoprene units and has a Tg of about -16°C. Another example of a high Tg rubber is a solution-polymerized styrene/butadiene copolymer rubber containing 12 weight percent styrene, a vinyl content of about 40 weight percent, a Tg of -45°C and a Mooney viscosity (ML1+4) at 100°C of 90. Another high Tg rubber is a styrene/isoprene/butadiene terpolymer rubber containing 20 weight percent styrene, 40 weight percent isoprene and 40 percent butadiene, a Tg of -42°C and a Mooney viscosity at 100°C of 90. Yet another high Tg rubber is an emulsion-polymerized polybutadiene rubber characterized by the weight percent of 1,4-bonds ranging from 65 to 70 percent, 15 to 20 weight percent of the units of a vinyl 1,2-structure and 8 to 15 weight percent of its units of a cis 1,4-structure. Such emulsion-polymerized polybutadiene has a Tg of -65°C and Mooney viscosity (ML 1+4) at 100°C of about 65.

[0009] Additional examples of high Tg rubbers are emulsion-polymerized styrene/butadiene copolymer rubbers characterized by a weight percent of from 23.5 to 40 weight percent styrene. For example, an emulsion-polymerized styrene/butadiene copolymer rubber having 23.5 weight percent styrene typically has a Tg of about -55°C and a Mooney viscosity (ML 1+4) at 100°C of about 50. An emulsion-polymerized styrene/butadiene copolymer rubber having 40 weight percent styrene typically has a Tg of about -35°C and a Mooney viscosity (ML 1+4) at 100°C of about 50.

[0010] The tire of the present invention is comprised of a tread compound containing from 15 to 50 phr of a resin selected from the group consisting of hydrocarbon resins, phenol/acetylene resins, rosin-derived resins and mixtures thereof. Preferably, the rubber contains from 15 to 30 phr of the resin.

[0011] Representative hydrocarbon resins include coumarone-indene resins, petroleum resins, terpene polymers and mixtures thereof.

[0012] Coumarone-indene resins are commercially available in many forms with melting points ranging from 10°C to 160°C (as measured by the ball-and-ring method). Preferably, the melting point ranges from 30 to 100°C. Coumarone-indene resins are well known. Various analysis indicate that such resins are largely polyindene; however, typically contain random polymeric units derived from methyl indene, coumarone, methyl coumarone, styrene and methyl styrene. Representative examples of commercially available coumarone-indene resins are those marketed under the designation CUMAR® from Nalcochem. These resins have a number of designations, some of which are listed below:

Resin	Softening Point °C	Specific Gravity @ 25°C	Molecular Weight No. Average
R-3	130	1.13	515
LX-509	157	1.14	700
R-11	112	1.09	700
R-13	105	1.12	460
R-17	70	1.10	500
R-21	45	1.05	450
R-29	25	1.08	420

[0013] The softening point was determined by ASTM E-28. The specific gravity was determined by ASTM D-71. The molecular weight number average was determined by ASTM D-3536.

[0014] Petroleum resins are commercially available with softening points ranging from 10°C to 120°C. Preferably, the softening point ranges from 30 to 100°C. Suitable petroleum resins include both aromatic and nonaromatic types. Several types of petroleum resins are available. Some resins have a low degree of unsaturation and high aromatic content, whereas some are highly unsaturated and yet some contain no aromatic structure at all. Differences in the resins are largely due to the olefins in the feedstock from which the resins are derived. Conventional derivatives in such resins include dicyclopentadiene, cyclopentadiene, their dimers and diolefins such as isoprene and piperylene. A representative example of such a petroleum resin is Wingtack 95, which is commercially available from The Goodyear Tire & Rubber Company.

ber Company.

[0015] Terpene polymers are commercially produced from polymerizing a mixture of beta pinene in mineral spirits. The resin is usually supplied in a variety of melting points ranging from 10°C to 135°C. Commercially available terpene polymers are available from Glidden under the designation CMP-361 and Schenectady Chem Co under the designation SP-560.

[0016] Phenol/acetylene resins may be used. Phenol/acetylene resins may be derived by the addition of acetylene to butyl phenol in the presence of zinc naphthlate. Additional examples are derived from alkylphenol and acetylene. A representative example of the latter is a resin that is commercially available from GAF of New York, New York, under the designation KORESIN™. This particular resin has a melting point of from 110°C to 130°C.

[0017] Resins derived from rosin and derivatives may be used in the present invention. Gum and wood rosin have much the same composition, although the amount of the various isomers may vary. They typically contain about 10 percent by weight neutral materials, 53 percent by weight resin acids containing two double bonds, 13 percent by weight of resin acids containing one double bond, 16 percent by weight of completely saturated resin acids and 2 percent of dehydroabietic acid which contains an aromatic ring but no unsaturation. There are also present about 6 percent of oxidized acids. Representative of the diunsaturated acids include abietic acid, levopimaric acid and neoabietic acid. Representative of the monounsaturated acids include dextropimaric acid and dihydroabietic acid. A representative saturated rosin acid is tetrahydroabietic acid. A commercially available rosin-derived resin is sold under the designation Westvaco Resin-90 from Westvaco Chemical Co.

[0018] The term "phr" as used herein, and according to conventional practice, refers to "parts by weight of a respective material per 100 parts by weight of total rubber or elastomer in the compound."

[0019] The pneumatic tire of the present invention may contain a siliceous filler. The siliceous fillers or pigments include pyrogenic and precipitated silica. The siliceous pigments are preferably precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

[0020] The silica filler, if used, may be added in amounts ranging from 10 to 250 phr. Preferably, the silica is present in an amount ranging from 15 to 80 phr.

[0021] Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930).

[0022] The silica may also be typically characterized by having a dibutyl phthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

[0023] The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

[0024] Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa AG with, for example, designations VN2 and VN3, etc. The PPG Hi-Sil silicas are currently preferred.

[0025] If silica is optionally added to the compound, one may add silica coupling agents to promote the adhesion between the rubber and silica. Representative coupling agents include organosilanes such as 3,3' bis(triethoxysilylpropyl) tetrasulfide. Silica coupling agents are generally used in amounts ranging from .1 to 20 phr. Specific examples of such organosilanes are disclosed in U.S. Patent 4,128,438 incorporated by reference in its entirety.

[0026] It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing oils, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozo-